



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : B01J 23/50, 37/02, 37/06, C07D 301/10		A1	(11) International Publication Number: WO 00/15334 (43) International Publication Date: 23 March 2000 (23.03.00)
<p>(21) International Application Number: PCT/EP99/06722</p> <p>(22) International Filing Date: 9 September 1999 (09.09.99)</p> <p>(30) Priority Data: 60/100,195 14 September 1998 (14.09.98) US</p> <p>(71) Applicant: SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).</p> <p>(72) Inventor: LOCKEMEYER, John, Robert; 3403 Stoney Mist Drive, Sugar Land, TX 77479 (US).</p>		<p>(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	
<p>(54) Title: PROCESS FOR PREPARING CATALYSTS WITH IMPROVED CATALYTIC PROPERTIES</p> <p>(57) Abstract</p> <p>This invention relates to a process for depositing one or more catalytically reactive metals on a carrier, said process comprising selecting a carrier and depositing a catalytically effective amount of one or more catalytically reactive metals on the carrier, the deposition effected by submersing the carrier in an impregnation solution wherein the hydrogen ion activity of the impregnation solution has been lowered. The invention further relates to catalysts made by the process. In the examples silver and a promotor are deposited on an alumina carrier in the presence of tetraethylammonium hydroxide; the catalysts are used for the preparation of ethylene oxide.</p>			

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PROCESS FOR PREPARING CATALYSTS WITH
IMPROVED CATALYTIC PROPERTIES

Field of the Invention

The invention relates to a process for the preparation of catalysts with improved catalytic properties, particularly improved initial activity, 5 initial selectivity and/or activity and/or selectivity performance over time.

Background of the Invention

Numerous methods are known for the deposition of catalytically reactive metals on a carrier in order to 10 manufacture catalysts. For example, U.S. Patent No. 3,972,829, issued August 3, 1976, discloses a method for distributing catalytically reactive metallic components on carriers using an impregnating solution of catalyst precursor compound and an organic thioacid or a 15 mercaptocarboxylic acid. U.S. Patent No. 4,005,049, issued January 25, 1977, teaches the preparation of a silver/transition metal catalyst useful in oxidation reactions. International publication WO 96/23585, published August 8, 1996, teaches that boosting the 20 amount of alkali metal promoter in a silver solution results in improved properties.

Literature also warns against certain methods. US 4,908,343, issued March 13, 1990, warns against having a silver solution which has a strong acidity or basicity 25 as the strongly acid or base solution would leach any leachable impurities from the carrier, becoming part of the silver catalyst in amounts which adversely affects the performance of the catalyst in an oxidation reaction.

It has surprisingly been found that the metal 30 deposition and catalytic properties of a catalyst may be

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greatly improved by lowering the hydrogen ion activity of the impregnation solution.

Summary of the Invention

According to one embodiment of the invention, there
5 is provided a process for preparing a catalyst, including
the steps of:

- selecting a carrier; and
- depositing one or more catalytically reactive metals
10 and optionally promoting materials on the carrier;
the deposition being effected by an impregnation solution
the hydrogen ion activity of which is lowered.

In particular the hydrogen ion activity of the
impregnation solution is lowered by the addition of a
base.

15 Preferably the hydrogen ion activity of the
impregnation solution is lowered by at least a factor of
five. More preferably the hydrogen ion activity of the
impregnation solution is lowered by a factor of from five
to a thousand. In an aqueous medium, these figures
20 correspond to raising the pH by numbers of 0.5 and 0.5-3
respectively.

25 In a further embodiment, the catalyst to be prepared
in the process according to the invention is suitable for
the vapour phase epoxidation of olefins and the
impregnation solution contains silver.

Description of the Preferred Embodiments

It has been found that lowering the hydrogen ion
activity of the impregnation solution used to deposit
catalytically reactive metals on a carrier provides
30 catalysts which have improved catalytic properties, such
as activity, selectivity and the activity and/or
selectivity performance over time. The process is
believed to work to improve the properties of most
catalysts wherein metal is deposited on a carrier by use
35 of an impregnation solution.

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Catalysts are commonly made by depositing a catalytically effective amount of one or more catalytically reactive metals on a carrier to make a catalyst precursor. Typically, the carrier is 5 impregnated with metal or compound(s), complex(es) and/or salt(s) sufficient to deposit or impregnate the catalytically reactive material. As used herein, "catalytically effective amount" means an amount of metal that provides a measurable catalytic effect.

10 The impregnated carrier, or catalyst precursor, is dried in the presence of an atmosphere which also reduces the catalytic metal. Drying methods known in the art include steam drying, drying in an atmosphere with a controlled oxygen concentration, drying in reducing 15 atmospheres, air drying, and staged drying using a suitable ramped or staged temperature curve.

20 In the process of the invention, improvement in the catalytic properties are seen when the metal deposition is effected by use of an impregnation solution whose hydrogen ion activity has been lowered. "Hydrogen ion activity" as used herein is the hydrogen ion activity as measured by the potential of a hydrogen ion selective electrode. As used herein, a solution with "lowered" 25 hydrogen ion activity refers to a solution whose hydrogen activity has been altered by the addition of a base, such that the hydrogen ion activity of the altered solution is lowered compared to the hydrogen ion activity of the same solution in an unaltered state. The base selected to alter the solution may be chosen from any base or 30 compound with a pK_b higher than the original impregnation solution. It is particularly desirable to choose a base which does not alter the formulation of the impregnation solution; i.e., which does not alter the desired metals concentration in the impregnation solution and deposited 35 on the carrier. Organic bases will not alter the

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impregnation solution metals concentrations, examples of which are tetraalkylammonium hydroxides and 1,8-bis-(dimethylamino)-naphthalene. If changing the metals concentration of the impregnation solution is not a concern, metal hydroxides may be used.

When the impregnation solution is at least partially aqueous, an indication of the change in the hydrogen activity may be measured with a pH meter, with the understanding that the measurement obtained is not pH by a true, aqueous definition. "Measured pH" as used herein shall mean such a non-aqueous system pH measurement using a standard pH probe. Even small changes in the "measured pH" from the initial impregnation solution to that with added base are effective and improvements in catalytic properties continue as the "measured pH" change increases with base addition. High base additions do not seem to adversely affect catalyst performance; however, high additions of hydroxides have been seen to cause sludging of the impregnation solution, creating manufacturing difficulties. When the base addition is too low, the hydrogen ion activity will not be affected.

As described, the process is effective in improving at least one of the catalytic properties of a catalyst wherein an impregnating solution is used to deposit or impregnate a catalytically reactive metal upon a carrier. "Improvement in catalytic properties" as used herein means the properties of the catalyst are improved as compared to a catalyst made from the same impregnation solution which has not had the hydrogen ion activity lowered. Catalytic properties include catalyst activity, selectivity, activity and/or selectivity performance over time, operability (resistance to runaway), conversion and work rate.

Further improvement in properties may be achieved by lowering the concentration of ionizable species present on the surface of the carrier prior to the deposition step. Carriers are commonly inorganic materials such as, 5 for example, alumina-, silica-, or titania-based compounds, or combinations thereof, such as alumina-silica carriers. Carriers may also be made from carbon-based materials such as, for example, charcoal, activated carbon, or fullerenes. Ionizable species typically 10 present on the inorganic type carriers include sodium, potassium, aluminates, soluble silicate, calcium, magnesium, aluminosilicate, cesium, lithium, and combinations thereof. Lowering the undesirable ionizable species concentration may be accomplished by any means 15 (i) which is effective in rendering the ionizable species ionic and removing that species, or (ii) which renders the ionizable species insoluble, or (iii) which renders the ionizable species immobile; however, use of aggressive media, such as acids or bases, is discouraged 20 as these media tend to dissolve the carrier, extract too much material from the bulk, and generate acidic or basic sites in the pores. Effective means of lowering concentration include washing the carrier; ion exchange; volatilizing, precipitating, or sequestering the 25 impurities; causing a reaction to make the ionizable species on the surface insoluble; and combinations thereof. Examples of wash and ion exchange solutions include aqueous and/or organic solvent-based solutions 30 which may also contain tetraethylammonium hydroxide, ammonium acetate, lithium carbonate, barium acetate, strontium acetate, crown ether, methanol, ethanol, dimethylformamide, and mixtures thereof. The formed carrier may be treated, or the materials used to form the carrier may be treated before the carrier is 35 manufactured. The formed carrier may be treated, or the

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5 materials used to form the carrier may be treated before the carrier is manufactured. When the carrier materials are treated before the carrier is formed, still further improvement may be seen by retreating the surface of the formed carrier. Following removal of the ionizable species, the carrier is optionally dried. When the removal process is by washing with an aqueous solution, drying is recommended.

10 By way of example, the process will be described in more detail for a catalyst suitable for the vapour phase production of epoxides, also known as an epoxidation catalyst.

15 First, a carrier is selected. In the case of an epoxidation the carrier is typically an inorganic material, such as, for example, an alumina-based carrier such as α -alumina.

20 In the case of α -alumina-containing carriers, preference is given to those having a specific surface area as measured by the B.E.T. method of from 0.03 m^2/g to 10 m^2/g , preferably from about 0.05 m^2/g to 5 m^2/g , more preferably from 0.1 m^2/g to 3 m^2/g , and a water pore volume as measured by conventional water absorption techniques of from 0.1 to 0.75 ml/g by volume. The B.E.T. method for determining specific surface area is described in detail in Brunauer, S., Emmett, P. Y. and Teller, E., J. Am. Chem. Soc., 60, 309-16 (1938).

25 Certain types of α -alumina containing carriers are particularly preferred. These α -alumina carriers have relatively uniform pore diameters and are more fully characterized by having B.E.T. specific surface areas of from 0.1 m^2/g to 3 m^2/g , preferably from 0.1 m^2/g to 2 m^2/g , and water pore volumes of from 0.10 to 0.55 ml/g. Manufacturers of such carriers include Norton Chemical

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Process Products Corporation and United Catalysts, Inc.
(UCI).

The carrier is typically impregnated with metal compound(s), complex(es) and/or salt(s) dissolved in a suitable solvent sufficient to cause the desired deposition on the carrier. If excess of impregnation solution is used, the impregnated carrier is subsequently separated from the impregnation solution and the deposited metal compound is reduced to its metallic state. In the process of the invention, the hydrogen ion activity of the impregnation solution is lowered prior to beginning the deposition or impregnation process. The typical impregnation solution for an epoxidation catalyst begins quite basic, so a strong base is used to further lower the hydrogen ion activity. It is particularly desirable to chose a base which does not alter the formulation of the impregnation solution, such as organic bases; however, if changing the metals concentration of the impregnation solution is not a concern, metal bases may be used. Examples of strong bases include alkylammonium-hydroxides, such as tetraethylammonium hydroxide, and metal hydroxides, such as lithium hydroxide and cesium hydroxide. Combinations of bases may also be used. In order to maintain the desired impregnation solution formulation and metal loading, an organic base such as tetraethylammonium hydroxide is preferred. These desired level of base additions typically result in a "measured pH" change ranging from about 0.5 to about 3, realizing that the "measured pH" is not a true pH since the impregnation system is not aqueous.

If an excess of impregnation solution is used, the impregnated carrier is subsequently separated from the solution before the deposited metal compound is reduced. Promoters, components which work effectively to provide

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an improvement in one or more of the catalytic properties of the catalyst when compared to a catalyst not containing such components, may also be deposited on the carrier either prior to, coincidentally with, or 5 subsequent to the deposition of the catalytically reactive metal. —

If the above described ionizable species concentration lowering step is utilized, the concentration of the ionizable species present on the 10 carrier surface is lowered prior to the deposition or impregnation step. Ionizable species present on an α -alumina carrier, for example, typically include sodium, potassium, aluminates, soluble silicates, calcium, magnesium, aluminosilicates, and combinations thereof. 15 It has been found that silicates, and certain other anions, are particularly undesirable ionizable species in an epoxidation catalyst. The solubilization rate of silicates may be measured by inductively coupled plasma (ICP) techniques and the amount of silicon species on a 20 surface may be measured by x-ray photoelectron spectroscopy (XPS); however, since sodium is soluble in the same solutions that silicates are soluble in, the solubilization rate of sodium becomes a simpler check of the ionic species removal. Another measurement technique 25 is to measure the electrical conductivity of the treatment solution.

The concentration of the undesirable ionizable species may be lowered by any means which is effective in rendering the ionizable species ionic and removing that 30 species, or rendering the ionizable species insoluble, or rendering the ionizable species immobile. Means effective in lowering the concentration of the undesirable ionizable species on the surface include washing, ion exchange, volatilization, precipitation,

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sequestration, impurity control and combinations thereof. Cleansing of an alumina-based carrier may be efficiently and cost-effectively accomplished by washing or ion exchange. Any solution capable of reducing the 5 concentration of the undesirable ionizable species — present, particularly the anionic ionizable species, and most particularly ionizable silicates, may be used. The carrier is then optionally dried; however, when the removal process is by washing, drying is recommended.

10 The carrier is impregnated with metal ions or compound(s), complex(es) and/or salt(s) dissolved in a suitable solvent sufficient to cause the desired deposition on the carrier. When silver is the deposition material, a typical deposition is from 1 to 40 wt%, 15 preferably from 1 to 30 wt% of silver, basis the weight of the total catalyst. The impregnated carrier is subsequently separated from the solution and the deposited metal(s) compound is reduced to metallic silver.

20 One or more promoters may be deposited either prior to, coincidentally with, or subsequent to the deposition of the metal. Promoters for epoxidation catalysts are typically selected from sulphur, phosphorus, boron, fluorine, Group IA through Group VIII metals, rare earth 25 metals, and combinations thereof. The promoter material is typically compound(s) and/or salt(s) of the promoter dissolved in a suitable solvent.

30 For olefin epoxidation oxide catalysts, Group IA metals are typically selected from potassium, rubidium, cesium, lithium, sodium, and combinations thereof; with potassium and/or cesium and/or rubidium being preferred. Even more preferred is a combination of cesium plus at least one additional Group IA metal, such as cesium plus potassium, cesium plus rubidium, or cesium plus lithium. 35 Group IIA metals are typically selected from magnesium,

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calcium, strontium, barium, and combinations thereof, Group VIII transition metals are typically selected from cobalt, iron, nickel, ruthenium, rhodium, palladium, and combinations thereof; and rare earth metals are typically selected from lanthanum, cerium, neodymium, samarium, — gadolinium, dysprosium, erbium, ytterbium, and mixtures thereof. Non-limiting examples of other promoters include perrhenate, sulfate, molybdate, tungstate, chromate, phosphate, borate, sulfate anion, fluoride anion, oxyanions of Group IIIB to VIB, oxyanions of an element selected from Groups III through VIIB, alkali(ne) metal salts with anions of halides, and oxyanions selected from Groups IIIA to VIIA and IIIB through VIIB. The amount of Group IA metal promoter is typically in the range of from 10 ppm to 1500 ppm, expressed as the metal, by weight of the total catalyst, and the Group VIIb metal is less than 3600 ppm, expressed as the metal, by weight of the total catalyst.

Other embodiments of the invention provide catalysts made by the processes just described.

The resulting epoxidation catalysts just described are used for the vapour phase production of epoxides, especially ethylene oxide. A typical epoxidation process involves loading catalysts into a reactor. The feedstock to be converted, typically a mixture of ethylene, oxygen, carbon dioxide, nitrogen and ethyl chloride, is passed over the catalyst bed at elevated pressure and temperature. The catalyst converts the feedstock to an outlet stream product which contains ethylene oxide. Nitrogen oxides (NO_x) may also be added to the feedstock to boost catalyst conversion performance.

The following Examples will illustrate the invention.

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Examples

Carriers

Table I shows the carriers used for the Examples.

TABLE I

Carrier	A	B
B.E.T. Surface Area (m ² /g) ^(a)	0.84	0.97
Water Absorption (%)	39.7	46.2
Crush Strength (kg) ^(b)	6.53	8.07
Total Pore Volume (ml/g) ^(c)	0.408	0.460
Median Pore Diameter (microns) ^(c)	1.8	2.7
SiO ₂ (%w)	0.5	0.8
Bulk Acid-Leachable Na (ppmw)	438	752
Bulk Acid-Leachable K (ppmw)	85	438
Bulk Acid-Leachable Ca (ppmw)	207	508
Bulk Acid-Leachable Al (ppmw)	744	1553
Bulk Acid-Leachable SiO ₂ (ppmw)	808	1879
alpha-Alumina (% w)	Bal	Bal

^a Method of Brunauer, Emmett and Teller, loc. cit.

5

^b Flat Plate Crush Strength, single pellet.

10

^c Determined by mercury intrusion to 3.8×10^8 Pa using Micromeritics Autopore 9200 or 9210 (130° contact angle, 0.473 N/m surface tension of Hg).

15

Carrier Washing Procedures for Examples 1, 3, 4, 5, 6, 7,
7b, 8, 9, 11

20

Carrier washing was carried out by immersing 100 grams of carrier in 300 grams of boiling de-ionized water for 15 minutes. The carrier was then removed and placed in a fresh 300 grams of boiling water for another 15 minutes. This procedure was repeated once more for a total of three immersions, at which point the carrier was separated from the water and dried in a well ventilated oven at 150 °C for 18 hours. The dried carrier was then used for preparation of a catalyst by the procedures outlined in the following Examples.

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Impregnation Solution

A silver-amine-oxalate stock solution was prepared by the following procedure:

5 415 g of reagent-grade sodium hydroxide were dissolved in 2340 ml de-ionized water and the temperature was adjusted to 50 °C.

1699 g high purity "Spectropure" silver nitrate were dissolved in 2100 ml de-ionized water and the temperature was adjusted to 50 °C.

10 The sodium hydroxide solution was added slowly to the silver nitrate solution, with stirring, while maintaining a solution temperature of 50 °C. The mixture was stirred for 15 minutes, then the temperature was lowered to 40 °C.

15 Water was removed from the precipitate created in the mixing step and the conductivity of the water, which contained sodium and nitrate ions, was measured. An amount of fresh deionized water equal to the amount removed was added back to the silver solution. The 20 solution was stirred for 15 minutes at 40 °C. The process was repeated until the conductivity of the water removed was less than 90 µmho/cm. 1500 ml fresh deionized water was then added.

25 630 g of high-purity oxalic acid dihydrate were added in approximately 100 g increments. The temperature was kept at 40 °C and the pH was kept above 7.8.

Water was removed from the mixture to leave a highly concentrated silver-containing slurry. The silver oxalate slurry was cooled to 30 °C.

30 699 g of 92 %w ethylenediamine (8% de-ionized water) was added while maintaining a temperature no greater than 30 °C. The resulting solution contained approximately 27-33 %w silver.

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Enough 45 %w aqueous CsOH and water was added to this solution to give a finished catalyst having 14.5 %w silver and a desired cesium loading (see Examples).

pH Measurement Procedures

5 Silver solution pH measurements were done using a— Metrohm model 744 pH meter, employing a model 6.0220.100 combination electrode and a Pt 100 model 6.1110.100 resistance thermometer for temperature compensation. The meter was calibrated with commercially available buffer
10 solutions before each use. In a typical measurement, a 50 ml aliquot of the doped silver solution to be used for a catalyst impregnation was filtered into a 100 ml glass beaker through a 2 micron filter attached in-line to a plastic syringe. The pH probe was lowered into the
15 magnetically stirred solution, and the reading obtained after 3 minutes was recorded as the equilibrated pH. The probe was cleaned between each measurement with deionized water, and checked for calibration. Special care was taken to prevent accumulation of AgCl solids on the
20 electrode membrane. Such accumulation was removed by soaking the probe in ammonium hydroxide solution, as recommended by the manufacturer.

Example 1a (Comparative - Base Case Carrier A, Washing)

25 A catalyst precursor was prepared from Carrier A by first subjecting the carrier to carrier washing. Following the wash, approximately 30 grams of washed Carrier A were placed under a 3.33 kPa vacuum for 1 minute at ambient temperature. Approximately 50 grams of the impregnating solution was then introduced to
30 submerge the carrier, and the vacuum was maintained at 3.33 kPa for an additional 3 minutes. The cesium target was 450 ppm/gram finished catalyst. The vacuum was then released and the excess impregnating solution was removed from the catalyst pre-cursor by centrifugation at 500 rpm
35 for two minutes. The catalyst pre-cursor was then dried

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while being shaken at 240 °C for 4 minutes in a stream of air flowing at 11.3 m³/hr.

Example 2a (Comparative - Base Case Carrier A, No Washing)

5 Carrier A was impregnated as described in Example 1a; however, the carrier was not subjected to carrier washing. The cesium target was 400 ppm/gram finished catalyst.

Example 3

10 Carrier A was subjected to carrier washing and impregnation as described in Example 1a. The cesium target was 500 ppm/gram finished catalyst. In addition, 35% aqueous tetraethylammonium hydroxide (TEAH) was added to the stock impregnation solution at a target of 15 117.8 micromoles OH⁻/ml Ag solution, to lower the hydrogen ion activity to a "measured pH" of 13.7.

Example 4

20 A catalyst was prepared in the same manner as that in Example 1. The cesium target was 720 ppm/gram finished catalyst. In addition, TEAH was dissolved in water and added to the stock solution at a target of 25 117.8 micromoles OH⁻/ml Ag, to lower the hydrogen activity to a "measured pH" of 13.2, and NH₄ReO₄ was dissolved in water and added to the stock solution to provide 1.5 micromoles Re/gram finished catalyst.

Example 5

30 500 g of Carrier A were subjected to carrier washing then immersed in 1500 ml of boiling 5 %w aqueous TEAH for 15 minutes. The carrier was then separated from the solution and washed repeatedly with boiling water according to the Carrier Washing Procedure. The carrier was then used to prepare a catalyst according to the procedure described in Example 2 with a "measured pH" of 35 13.6. The cesium target was 400 ppm/gram finished catalyst.

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Example 6

Carrier A was subjected to carrier washing and impregnation as described in Example 1. The cesium target was 430 ppm/gram finished catalyst. In addition, 5 LiNO₃ and LiOH were added to the stock impregnation solution, lowering the hydrogen ion activity to a "measured pH" of 12.5.

Example 7

Carrier A was subjected to carrier washing and 10 impregnation as described in Example 1. The cesium target was 450 ppm/gram finished catalyst. In addition, LiOH was dissolved in water and added to the stock impregnation solution to lower the hydrogen ion activity to a "measured pH" of 13.2.

15 Example 8a (Comparative)

Carrier A catalyst was impregnated as described in Example 6; however, the carrier was not subjected to carrier washing. The cesium target was 400 ppm/gram finished catalyst.

20 Example 9a (Comparative)

A silver solution was prepared as described in Example 6. The "measured pH" of the solution was 13.2. CO₂ was bubbled slowly through the solution until the "measured pH" was 12.0. The solution was used to prepare 25 a catalyst as described in Example 1.

Example 10

A catalyst was prepared in the same manner as that in Example 1. The cesium target was 650 ppm/gram finished catalyst. In addition, LiOH was dissolved in water and 30 added to the stock impregnation solution to lower the hydrogen ion activity to a "measured pH" of 13.2 and NH₄ReO₄ was dissolved in water and added to the stock impregnation solution to provide 1.5 micromoles Re/gram finished catalyst.

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Example 11a (Comparative - Base Case Carrier B, Washing)

Carrier B was used to prepare a catalyst as described in Example 1. The cesium target was 450 ppm/gram catalyst.

5 Example 12a (Comparative - Base Case Carrier B, No -
Washing)

Carrier B was impregnated as described in Example 1; however, the carrier was not subjected to carrier washing. The cesium target was 500 ppm/gram finished catalyst.

10 Example 13

Carrier B was used to prepare a catalyst as described in Example 1. The cesium target was 550 ppm/gram finished catalyst. In addition, LiOH was dissolved in water and added to the stock impregnation solution to lower the hydrogen ion activity to a "measured pH" of 13.2.

15 Example 14

20 A catalyst was prepared as described in Example 13; however, the carrier was not subjected to carrier washing. The cesium target was 500 ppm/gram finished catalyst.

25 The catalysts of Examples 1a-14 were used to produce ethylene oxide from ethylene and oxygen. 3 to 5 grams of crushed catalyst were loaded into a 6.35 mm inside diameter stainless steel U-shaped tube. The U tube was immersed in a molten metal bath (heat medium) and the ends were connected to a gas flow system. The weight of the catalyst used and the inlet gas flow rate were adjusted to 30 achieve a gas hourly space velocity of 6800 ml of gas per ml of catalyst per hour. The inlet gas pressure was 14500 kPa.

35 The gas mixture passed through the catalyst bed (in a once-through operation) during the entire test run (including start-up) consisted of 25% ethylene, 7.0%

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oxygen, 5% carbon dioxide, 63% nitrogen, and 2.0 to 6.0 ppmv ethyl chloride.

The initial reactor (heat medium) temperature was 180 °C. The temperature was ramped at a rate of 10 °C per 5 hour from 180 °C to 225 °C, and then adjusted so as to — achieve a constant ethylene oxide level of 1.5 %v in the outlet gas stream. Performance data at this conversion level are usually obtained when the catalyst has been on stream for a total of at least 1-2 days. Due to slight 10 differences in feed gas composition, gas flow rates, and the calibration of analytical instruments used to determine the feed and product gas compositions, the measured selectivity and activity of a given catalyst may vary slightly from one test run to the next.

15 The initial performance values for selectivity at 1.5% ethylene oxide were measured and are reported in Table II.

TABLE II. Performance Characteristics of Catalysts

Example	Carrier	Pre-Impregnation Condition	Base Addition	Impregnating Solution "measured pH"	Selectivity (%)	Temperature (°C)
1a	A	water wash	none	11.2	82.7	229
2a	A	no wash	none	11.2	81.3	237
3	A	water wash	TEAH	13.7	82.7	225
4	A	water wash	TEAH	13.2	89.4	245
5	A	TEAH wash + water wash	TEAH	13.6	82.7	222
6	A	water wash	LiNO ₃ + LiOH	12.5	82.7	225
7	A	water wash	LiOH	13.2	82.7	227
8	A	no wash	LiOH	13.2	82.0	227
9a	A	water wash	LiOH + CO ₂	12.0	82.8	231
10	A	water wash	LiOH	13.2	86.2	234
11a	B	water wash	none	11.2	82.5	226
12a	B	no wash	none	11.2	82.0	232
13	B	water wash	LiOH	13.2	82.9	226
14	B	no wash	LiOH	13.2	83.3	230

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It can be seen that significant improvement in catalyst properties are seen when the hydrogen ion activity of the deposition solution is lowered. This effect is not specific for a certain carrier, as 5 illustrated in the Example where two different carriers exhibit improvements by increasing "measured pH" of the impregnating solution. This also holds true for a drastically modified carrier, as in Example 5, where Carrier A has been extracted with a strongly basic 10 solution. Furthermore, the converse is shown to be true when the solution is "forced" back to a more acidic pH, as seen in Example 9a. In these examples it is shown that a more acidic pH (increasing hydrogen ion activity) is detrimental to the resulting catalyst performance, but 15 this loss can be reversed by rejuvenating the pH of the system. Even further improvement is seen when the carrier is washed before the catalytic metal is deposited on the carrier. It is also evident that the phenomenon of the pH effect is not restricted to a particular catalyst formulation, as best illustrated in Examples 4 and 10, where a selectivity enhancing dopant, such as rhenium, is added to the impregnating solution.

It will be apparent to one of ordinary skill in the art that many changes and modifications may be made to 25 the invention without departing from its spirit or scope as set forth herein.

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C L A I M S

1. A process for preparing a catalyst, including the steps of:
 - selecting a carrier; and
 - depositing one or more catalytically reactive metals and optionally promoting materials on the carrier; the deposition being effected by an impregnation solution the hydrogen ion activity of which is lowered.
- 5 2. A process according to claim 1, characterized in that the hydrogen ion activity of the impregnation solution is lowered by addition of a base.
- 10 3. A process according to claim 1 or 2, characterized in that the hydrogen ion activity of the impregnation solution is lowered by at least a factor 5.
- 15 4. A process according to any one of claims 1-3, characterized in that a carrier is used the concentration of one or more ionizable species present on a surface of which is lowered.
- 20 5. A process according to claim 4, characterized in that said concentration of one or more ionizable species on the surface of the carrier is lowered by a means effective in rendering the ionizable species ionic and removing that species, or rendering the ionizable species insoluble, or rendering the ionizable species immobile.
- 25 6. A process according to claim 5 wherein said means is selected from washing, ion exchange, volatilization, precipitation, sequestration and combinations thereof.
7. A process according to any one of claims 1-6, characterized in that the catalyst is useful in the vapour phase production of epoxidation of olefins and the impregnation solution contains silver.

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8. A process according to claim 7, further comprising depositing one or more promoters selected from sulphur, phosphorus, boron, fluorine, Group IA through Group VIII metals, rare earth metals, and combinations thereof.
- 5 9. A process according to claim 7 or 8, characterized in that the Group IA metal is selected from potassium, rubidium, cesium, lithium, sodium, and combinations thereof, the Group IIA metal, when present, is selected from magnesium, calcium, strontium, barium, and combinations thereof, the Group VIIb metal, when present, is rhenium and the Group VIII metal, when present, is selected from cobalt, iron, nickel, ruthenium, rhodium, palladium, and combinations thereof.
- 10 10. A process for the catalytic epoxidation of an alkene with an oxygen containing gas, wherein a catalyst prepared according to the process of any one of claims 7-9 is used and at least one nitrogen oxide is added to the oxygen containing gas.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 99/06722

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01J23/50 B01J37/02 B01J37/06 C07D301/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B01J C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 361 500 A (MATHE TIBOR ET AL) 30 November 1982 (1982-11-30) claims 1-4,6 ---	1-3,7-9
A	FR 2 005 978 A (INSTITU CERCETARI PETROC) 19 December 1969 (1969-12-19) claims 1-3 example 1 -----	1-9

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

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- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 January 2000	20/01/2000
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Zuurdeeg, B

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 99/06722

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